1.0

1.1

1.25　1.4　1.6

4.5
50

2.8　2.5
3.2
3.6　2.2
4.0　2.0

1.8

MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF

LEVEL

Site Distribution - Studies of Rh Supported on Al_2O_3 -
An Infrared Study of Chemisorbed CO

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Washington, DC   20234

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER Technical Report #18	2. GOVT ACCESSION NO. AD-A084852	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Site Distribution - Studies of Rh Supported on Al2O3 - An Infrared Study of Chemisorbed CO.		5. TYPE OF REPORT & PERIOD COVERED
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) R. R. Cavanagh and J. T. Yates, Jr		8. CONTRACT OR GRANT NUMBER(s) N00014-80-F-0008, Mod. No. 00001
9. PERFORMING ORGANIZATION NAME AND ADDRESS Surface Science Division National Bureau of Standards Washington, DC 20234		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS N00014-79-F-0008
11. CONTROLLING OFFICE NAME AND ADDRESS		12. REPORT DATE May 1980
		13. NUMBER OF PAGES
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for Public Release; Distribution Unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

Preprint; to be published in J. Chem. Phys.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Chemisorption; CO; dispersion; extinction coefficient; infrared spectroscopy; rhodium

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

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S/N 0102-014-6601

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Site Distribution Studies of Rh Supported

on Al_2O_3 - An Infrared Study of Chemisorbed CO

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ABSTRACT

Using infrared spectroscopy, chemisorbed CO has been employed as a surface probe to observe differences in Rh site distributions on Al_2O_3-supported Rh. It has been found that higher loadings of Rh lead to Rh site distributions resembling those found on Rh (111) single crystals, whereas low Rh loadings produce isolated Rh sites preferentially. The isolated Rh sites yield infrared spectra characteristic of a species, $Rh(CO)_2$. Chemisorption of oxygen onto the CO-covered surface effectively eliminates crystalline Rh sites, leaving only the isolated Rh sites which maintain their bonding to CO as seen by infrared spectroscopy. Estimates of the infrared extinction coefficient for $Rh(CO)_2$ have been made. The results are consistent with data from other laboratories which indicate that the Rh is in a $Rh^{\delta+}$ oxidation state.

I. Introduction

Vibrational spectroscopic studies of chemisorbed molecules on metal films and on single crystal surfaces have been the subject of numerous investigations. The techniques employed have included transmission infrared spectroscopy (1,2) electron energy loss spectroscopy (EELS) (3), inelastic electron tunneling spectroscopy (IETS) (4), reflection-absorption infrared spectroscopy (RAIS) (5), and Raman spectroscopy (6). Assignment of the spectral features to vibrational modes is typically based on the spectra of gas phase molecules of known structure. Earlier work, performed using transmission infrared spectroscopy through supported metals, has also provided a foundation for spectral assignments in the other spectroscopies (7). It is now becoming possible to compare results on supported metals with results obtained on single crystals of the same metal, and in some cases agreement between the two areas has been good. A comparison of dispersed and single crystal metals containing chemisorbed species can lead to new insights concerning the nature of chemisorption sites in both areas.

In addition to their relationship to bulk metals, studies of dispersed metal systems offer a unique possibility not available in single crystal or metal film studies. As the loading of the metal is decreased on the support, the metal can (in principle) reach _atomic_ dispersion. Care must be taken in these cases to prevent metal atom agglomeration by operating at the lowest temperatures possible in the preparation of the supported metal. Since the chemical behavior of the highly dispersed metals can vary significantly from that found on bulk metals, a spectroscopic probe, such as infrared spectroscopy of chemisorbed species, is highly desirable if effective at low metal loading. Since

adsorbed CO exhibits a high extinction coefficient in the infrared, it may be considered an ideal chemisorption-probe of adsorbate-site geometry. The carbonyl stretching frequency is known to be a sensitive indicator of the degree of coordination of CO to chemisorption sites (8).

Previous work on Al_2O_3-supported rhodium has demonstrated dispersion-dependent catalytic activity (9). In this note we report the variation in spectral features observed for chemisorbed CO on Al_2O_3-supported rhodium samples as the metal loading is varied from 0.2% to 10.0% by weight.

II. Experimental

Dispersed Rh on Al_2O_3 (Degussa Al_2O_3-C) was produced by hydrogen reduction at 450 K of Rh^{III} from $RhCl_3 \cdot 3H_2O$ dispersed on the Al_2O_3 using procedures described previously (10). For 2.2% Rh, the BET surface area of the Rh plus the support was found on similar samples to be $\sim$ 55 m^2/g using N_2 physisorption. The Rh weight percent was varied from 0.2% to 10%, with the Rh/Al_2O_3-sample density in the IR cell ranging from .016 to .004 gm/cm^2. The reduced Rh samples were prepared and studied in a stainless steel infrared cell having CaF_2 windows. Careful attention was paid to eliminate hydrocarbon impurities. In this regard, a grease-free bakeable stainless steel ultra-high vacuum system equipped with a liquid nitrogen cooled zeolite pump and an ion pump was used in these experiments. The limiting pressure was $< 10^{-8}$ Torr. Infrared spectra were obtained from 4000 cm^{-1} to 1000 cm^{-1} using a Perkin-Elmer Model 180 infrared spectrometer.* The wavenumber scale was calibrated using $CO(g)$, $H_2O(g)$ and $CO_2(g)$ (11). The chemisorption of CO could be measured using volumetric uptake measurements, and estimates then made of IR extinction coefficient by comparison of the CO uptake with integrated spectral absorbances.

III. Results

A. CO Infrared Spectra

Three full-coverage infrared spectra for CO chemisorbed at 50 torr on Al_2O_3-supported Rh surfaces are shown in Figure 1 following evacuation. The infrared absorbance scale was normalized for the three spectra using the CO uptake as the normalizing factor. In this comparison, the loading of Rh on the Al_2O_3 support has been varied from 0.2% to 10.0% by weight. For these CO saturated surfaces, the number of CO molecules per Rh atom was estimated by a linear extrapolation of the integrated absorbance plotted against the ratio of chemisorbed CO molecules to Rh atoms as determined by uptake measurements. This procedure was necessary due to the influence of a large dead space correction at high CO pressures where the final increase in infrared intensity occurs. The data for the 0.2% Rh surface in which $\int \ln \frac{I_o}{I} d \nu_{CO}$ is plotted versus the CO/Rh ratio is shown in Figure 2. While this is not a strictly correct procedure where mixtures of chemisorbed CO species are involved, the method yields an index of CO capacity per Rh atom which is of qualitative value. For the three loadings studied, the CO/Rh ratio varied systematically: [0.2% Rh; CO/Rh = 1.9]; [2.2% Rh; CO/Rh = 1.2]; [10.0% Rh; CO/Rh = 0.5]. The value determined for the 2.2% sample is in good agreement with absolute coverage determination made on a similar sample using ^{13}C-NMR spectroscopy (12), which itself was shown to agree with similar extrapolation of IR intensity plotted against CO chemisorption uptake. The decrease observed in the CO/Rh ratio as the Rh loading is increased is expected as a consequence of the increase in average Rh crystallite size.

The assignment of the spectral features seen for chemisorbed CO on Rh/Al_2O_3 has been widely discussed since the pioneering work of Yang and Garland (13). Based on analogies with spectra measured for rhodium carbonyls (14), supported rhodium carbonyl complexes and their dissociation products (15,16), and on the general principles influencing the vibrational

frequency of the C-O bond for different modes of bonding in molecules
and on surfaces, the following assignment has been made (10).

The features at 2101 and 2030 cm^{-1} are assigned as the symmetric
and asymmetric modes of $Rh(CO)_2$ species which are spatially isolated
from other adsorption sites. This assignment is based on the observed
simultaneous development at constant wavenumber of the two spectral
features as CO coverage is increased, as well as on the observation of
a similar doublet for species known to contain a $Rh(CO)_2$ moiety (10).
The observation of a CO/Rh ratio of 1.9 for these species on the 0.2%
surface supports this assignment. The feature near 2060 cm^{-1} is assigned
to terminally-bond CO on Rh crystallites, while the 1860 cm^{-1} feature is
assigned to bridge-bonded CO, also on Rh crystallites. The purpose of
these studies at various Rh loadings on Al_2O_3 was to test the above
assignments, thereby gaining insight into the kinds of Rh sites available
on Al_2O_3 supported Rh surfaces.

B. O_2 Interaction with The Rh Surface

Following the establishment of a CO-saturated Rh surface for the
2.2% Rh surface, (P_{CO} = 50 Torr), the gas phase CO was pumped away and
O_2(g) was admitted at 310 K to a pressure of 100 Torr. The spectral
change shown in Figure 3 was complete within minutes. Readmission of
CO to the evacuated cell had little effect. Similar effects were observed
by Primet when Rh/Al_2O_3 surfaces were exposed to O_2 either prior to or
following CO adsorption (17).

It is therefore shown here that oxygen preferentially eliminates
both the terminal and bridged-CO species present on Rh crystallites,
but the the Rh $(CO)_2$ species are relatively unaffected. The exact role

of the oxygen is not clear. Whether simple CO displacement from the crystalline sites, followed by oxygen site-blockage to prevent CO readsorption is operative, or whether oxygen is actually able to change the dispersion of the Rh by disrupting crystallines cannot be determined from these IR studies alone. It is also possible that oxygen is able to oxidize chemisorbed CO to CO_2 on the Rh crystallites (16) at room temperature.

IV. Discussion

A. Assignment of CO Spectral Features to Rh Sites.

1. Isolated Rh Sites.

The dominance of the 2100 and 2030 cm^{-1} features in the 0.2% sample is in good agreement with assignment of these features to $Rh(CO)_2$ species. The CO/Rh ratio of 1.9 for this system can be taken as further confirmation of the presence of the two-CO per-metal-atom stoichiometry.

Similar doublet spectra for CO adsorbed on Rh/Al_2O_3 were obtained by Yao and Rothschild (18) following extensive high temperature treatment in O_2 prior to H_2 reduction. They attributed this to oxygen-induced dispersion of Rh crystallites. Recently, the decomposition of $Rh_6(CO)_{16}$ on Al_2O_3 has been studied using infrared techniques. In a well-done investigation (16), it was postulated that surface hydroxyls on Al_2O_3 are effective in converting the $Rh_6(CO)_{16}$ to a species in which the Rh^0 in the carbonyl is oxidized to Rh^I,
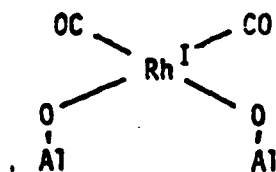
with the evolution of $H_2(g)$. The resulting spectrum exhibited only a doublet at 2105 cm^{-1} and 2040 cm^{-1}. Similar suggestions of the presence of an oxidized Rh have been made by Primet (17) in connection with the doublet spectrum.

In the work presented here, it is not possible to assign a definite oxidation state to the rhodium sites responsible for the formation of $Rh(CO)_2$. However, if we consider our supported Rh surfaces to consist of a mixture of $Rh^{\delta+}$ (isolated) sites and Rh_x^0 (crystallite) sites, then the special chemical properties of the $Rh^{\delta+}$ sites (as compared to Rh_x^0 sites) are rationalized. These special properties include:

(1) Formation of isolated $Rh(CO)_2$ species (10).

(2) Facile isotopic exchange at 200 K between $Rh(CO)_2$ and
*CO(g) (19), when Rh_x sites containing CO(ads) do not exchange.

(3) Lack of production of $Rh(CO)_2$ from H_2CO decomposition at the isolated sites (20).

(4) Lack of reaction with $O_2(g)$ at 310K at the isolated sites, seen in this work.

It has been found by infrared studies that here are at least 5 distinguishable distinguishable Al-OH sites on alumina surfaces (2,21). It would therefore not be surprising to find that the $Rh^{\delta+}$ species produced on the various hydroxyl sites differ slightly in their properties. The ~ 6 cm^{-1} shift of the doublet to lower

frequency on the 0.2% Rh surface, compared to the 2.2% Rh surface may reflect the fact that at low Rh loadings specific $Rh^{\delta+}$ species are produced at specific hydroxyl sites. The slight shift to lower frequency is consistent with a higher degree of rhodium electronic back donation to the CO, i.e., with $\delta+$ being smaller in the case of the low Rh loadings (22). As the Rh loading increases, hydroxyl sites with stronger oxidizing ability may be successively occupied within this model. The assignment of a degree of oxidation to the isolated $Rh^{\delta+}$ sites must await other studies.

2. Crystalline Rh Sites.

The CO infrared spectra shown for 2.2% and 10% Rh surfaces in Figure 1 include differing contributions from crystalline Rh sites. The relative intensity of

the 2060 cm^{-1} and the 1860 cm^{-1} feature increases as the loading of Rh increases. A significant comparison between these vibrational frequencies and the frequencies observed for CO on Rh (111) may be made. On Rh (111), at full-CO coverage, two CO modes are also observed at 2070 cm^{-1} and 1870 cm^{-1} (23). LEED studies of CO adsorption on Rh (111) had originally suggested that CO must exist in two kinds of sites at full coverage (24). In addition the kinetics of thermal desorption have been measured for CO on Rh (111), and the zero coverage heat of adsorption was determined to be 132 kJ mole^{-1} (24). The EELS results strongly suggest terminal and 2-fold bridging modes for CO in these sites.

The spectra shown in Figure 1 were obtained at a saturation coverage of CO. The spectral development as a function of CO coverage was followed during the uptake experiments. Shifts to higher frequency as a function of increasing coverage for the features associated with the crystallines were observed on the 2.2% and 10% samples. (The apparent decreased splitting of the doublet in going from 2.2% to 10% rhodium loading can be attributed to overlap with the 2060 cm^{-1} feature, rather than any shift in the location of the doublet). Coverage dependent frequency shifts are well known on single crystals (25) are and may arise from several kinds of inter- actions (25,26).

In contrast to the frequency shifts as a function of CO coverage observed for the two CO species on Rh crystallites, the doublet features associated with single Rh sites develop together without frequency shift. This observation has been inter- preted as evidence for the presence of isolated single Rh sites (10,13,18).

3. Infrared Extinction Coefficient for $Rh^{\delta+}(CO)_2$.

From Figure 2, the integrated CO intensity may be used to derive an extinction coefficient for the $Rh^{\delta+}(CO)_2$ species, using the linear portion of the curve. The

reasons for the curvature at low coverage are not understood at present. Duncan et al (27) has made a separate estimate of the CO extinction coefficient for the various types of CO by combining IR spectroscopy, volumetric uptake measurements, and ^{13}C-NMR measurements. His measurements were made on a 2.2% Rh/Al_2O_3 surface which is of substantially higher Rh loading than the 0.2% Rh/Al_2O_3 used in this work. Poor agreement exists between the two measurements [our work, $\epsilon_{Rh(CO)_2}$ = 13.8 x 10^6 mole^{-1}cm; NMR (27) work, $\hat{\epsilon}_{Rh(CO)_2}$ = 202 X 10^6 mole^{-1} cm]. When one defines the extinction coefficient as $\hat{\epsilon} = \frac{1}{nl}\int \ln \frac{I_o}{I} \frac{d\nu}{\nu_o}$, the magnitude of our $\hat{\epsilon}_{Rh(CO)_2}$ = 1.11 x 10^{-20} cm^2; NMR work (27), $\hat{\epsilon}_{Rh(CO)_2}$ = 15.7 x 10^{-20} cm^2. For comparison, gas phase CO has an extinction coefficient of ϵ = 5.8 x 10^6 mole^{-1} cm (22) [$\hat{\epsilon}_{CO}$ = 0.45 x 10^{-20} cm^2].

The differences in these measurements for chemisorbed CO may be due to the slightly different character of the $Rh^{\delta+}$ sites on samples having different loadings. This is suggested by the $\sim$ 6 cm^{-1} shift of the doublet to lower frequency on the 0.2% Rh surfaces compared to the 2.2% Rh surfaces which has been discussed above. The difference reported here is equivalent to a factor of $\sim$ 4 difference in the dipole derivative for the oscillator, $d\mu/dq$.

V. Summary

Infrared spectroscopy, combined with CO uptake measurements have clearly established the variation in Rh site distribution as a function of Rh loading on Al_2O_3. As the Rh loading is increased, the infrared spectra of chemisorbed CO become more characteristic of species on crystalline Rh sites. These species (terminal-CO and 2 fold bridge bonded CO) are identical in vibrational frequency to those observed on a Rh (111) single crystal surface. The dominance of $Rh^{\delta+}(CO)_2$ species at high Rh dispersions is demonstrated conclusively.

The reactivity with $O_2(g)$ of the crystalline sites is favored over the $Rh^{\delta+}$ sites, and preadsorption or postadsorption of oxygen may be used to eliminate the crystalline sites in-so-far as CO chemisorption in concerned.

Measurements of the infrared extinction coefficient for the $Rh^{\delta+}(CO)_2$ species have been made on the most dispersed Rh surfaces. When the measured extinction coefficient is expressed per CO adsorbate for this species, the infrared intensity is the same as for gas phase CO. This observation is in full accord with the suggestion made by Davenport in a recent paper (28) and with recent experimental work with bulk metals (29, 30).

We have demonstrated the power of infrared spectroscopy to discriminate different metal bonding sites using CO as a test molecule.

*The manufacturer and model of the infrared spectrometer are supplied to provide the reader with details of the experimental apparatus. No endorsement of this product by NBS is implied.

1. L. H. Little, Infrared Spectra of Adsorbed Species (Academic, London, 1966).

2. M. L. Hair, Infrared Spectroscopy in Surface Chemistry (Marcel Dekker, New York, 1967).

3. H. Ibach, M. Hopster, and B. Sexton, Appl. Surf. Sci. $\underline{1}$, 1 (1977). G. Dalmai-Imelik, J. C. Bertolini, and J. Rousseau, Surf. Sci. $\underline{63}$, 67 (1977). S. Andersson, Solid State Commun. $\underline{20}$, 229 (1976); 21, 75 (1977).

4. P. K. Hansma, W. C. Koska, and R. M. Laire, J. Am. Chem. Soc. $\underline{98}$, 6064 (1976).

5. J. Pritchard, M. L. Sims, Trans. Faraday Soc. $\underline{66}$, 427 (1970); J. Pritchard, T. Catterick, and R. K. Gupta, Surf. Sci. $\underline{53}$, 1 (1975). J. T. Yates, Jr. and D. A. King, Surf. Sci. $\underline{30}$, 601 (1972); J. T. Yates, Jr., R. G. Greenler, I. Rataczykowa, and D. A. King, ibid. $\underline{36}$, 739. (1973); A. M. Bradshaw and F. M. Hoffman, Surf. Sci. $\underline{72}$, 513 (1978).

6. T. Takenaka, Advances in Colloid and Interface Science $\underline{11}$, 291 (1979).

7. Vibrations in Adsorbed Layers. Proceedings of an International Conference June 12-14, 1978. Kernforschungsanlage Jülich, Germany. Ed. H. Ibach and S. Lehwald.

8. N. Sheppard and T. T. Nguyen, Advances in Infrared and Raman Spectroscopy $\underline{5}$ 67 (1978).

9. D. J. C. Yates, and J. H. Sinfelt, J. Catal. $\underline{8}$ 348 (1967).

10. J. T. Yates, Jr., T. M. Duncan, S. D. Worley, and R. W. Vaughan, J. Chem. Phys. $\underline{70}$ 1219 (1979).

11. E. K. Plyler, A. Danti, L. R. Blaine, E. D. Tidwell, Journal of Research Nat. Bur. Stand., Sect. $\underline{A64}$, 29 (1960).
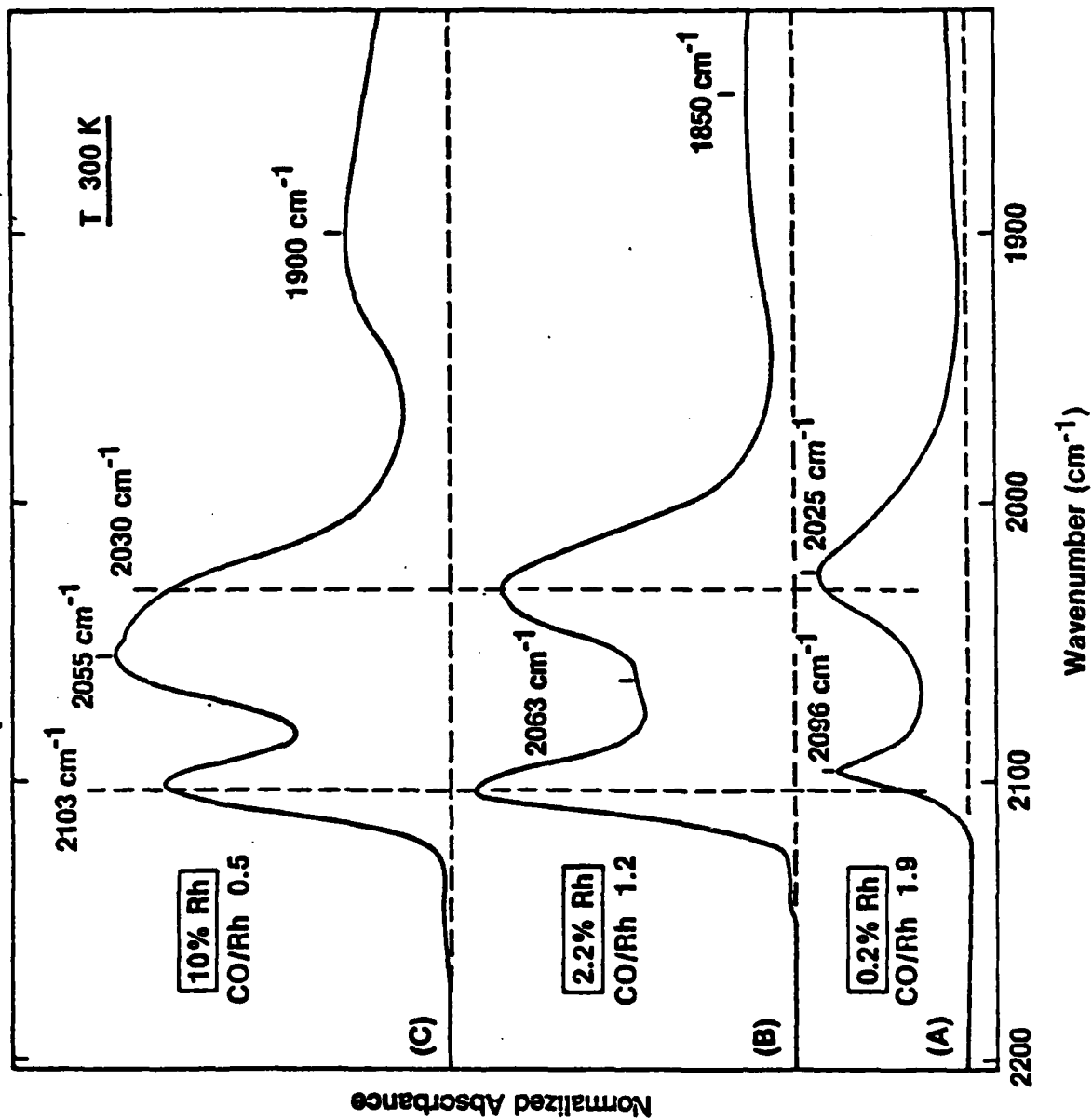
12. T. M. Duncan, J. T. Yates, Jr., and R. W. Vaughan, J. Chem. Phys. 71 3129 (1979).

13. A. C. Yang and C. W. Garland, J. Phys. Chem. 61 1504 (1957).

14. C. W. Garland and J. R. Wilt, J. Chem. Phys. 36 1094 (1962).

15. H. Knozinger, E. W. Thornton, and M. Wolf, J.C.S. Faraday I 75 1888 (1979).

16. A. K. Smith, F. Hugues, A. Theolier, J. M. Basset, R. Ugo, G. M. Zanderighi, J. L. Bilhou, V. Bilhou-Bougnol, and W. F. Graydon, Inorg. Chem. 18 3104 (1979).

17. M. Primet, J.C.S. Fara I. 74 2570 (1978).

18. H. C. Yao and W. G. Rothschild, J. Chem. Phys. 68 4774 (1978).

19. J. T. Yates, Jr., S. D. Worley, T. M. Duncan, and R. W. Vaughan, J. Chem. Phys. 70 1225 (1979).

20. J. T. Yates, Jr., T. M. Duncan, and R. W. Vaughan, J. Chem. Phys. 71 3908 (1979).

21. J. B. Peri, J. Phys. Chem. 69 220 (1965).

22. T. L. Brown and D. J. Darensbourg, Inorg. Chem. 6 971 (1967).

23. L. H. Dubois and G. A. Somorjai LBL Report 9280.

24. P. A. Thiel, E. D. Williams, J. T. Yates, Jr., and W. H. Weinberg, Surf. Sci. 84 54 (1979).

25. A. M. Bradshaw and F. Hoffman Surf. Sci. 72 513 (1978).

26. A. Crossley and D. A. King Surf. Sci. 68 528 (1977).

     G. D. Mahan and A. A. Lucas, J. Chem. Phys. 68 1344 (1978).

     M. Moskovits and J. E. Hulse, Surf. Sci. 78 397 (1978).

     M. Scheffler, Surf. Sci. 81 562 (1979).

27. T. M. Duncan, J. T. Yates, Jr., and R. W. Vaughan submitted to J. Chem. Phys.

28. J. W. Davenport to be published.

29. S. Andersson and J. W. Davenport, Sol. St. Commun. $\underline{28}$ 677 (1978).

30. B. N. J. Persson, Sol. St. Commun. $\underline{30}$ 163 (1979).

FIGURE CAPTIONS

Figure 1.   Full coverage infrared spectra of chemisorbed CO on

       Rh/Al_2O_3 A.) 0.2% Rh, B.) 2.2% Rh, C.) 10% Rh.

Figure 2.   Integrated absorbance of CO features as a function of

       quantity of CO chemisorbed for a 0.2% Rh/Al_2O_3 sample.

Figure 3.   Effect of O_2 on infrared spectrum of chemisorbed CO.

       A.) CO saturated sample of 2.2% Rh/Al_2O_3

       B.) Following exposure of sample A to 100 Torr of O_2

        with subsequent saturation by CO.

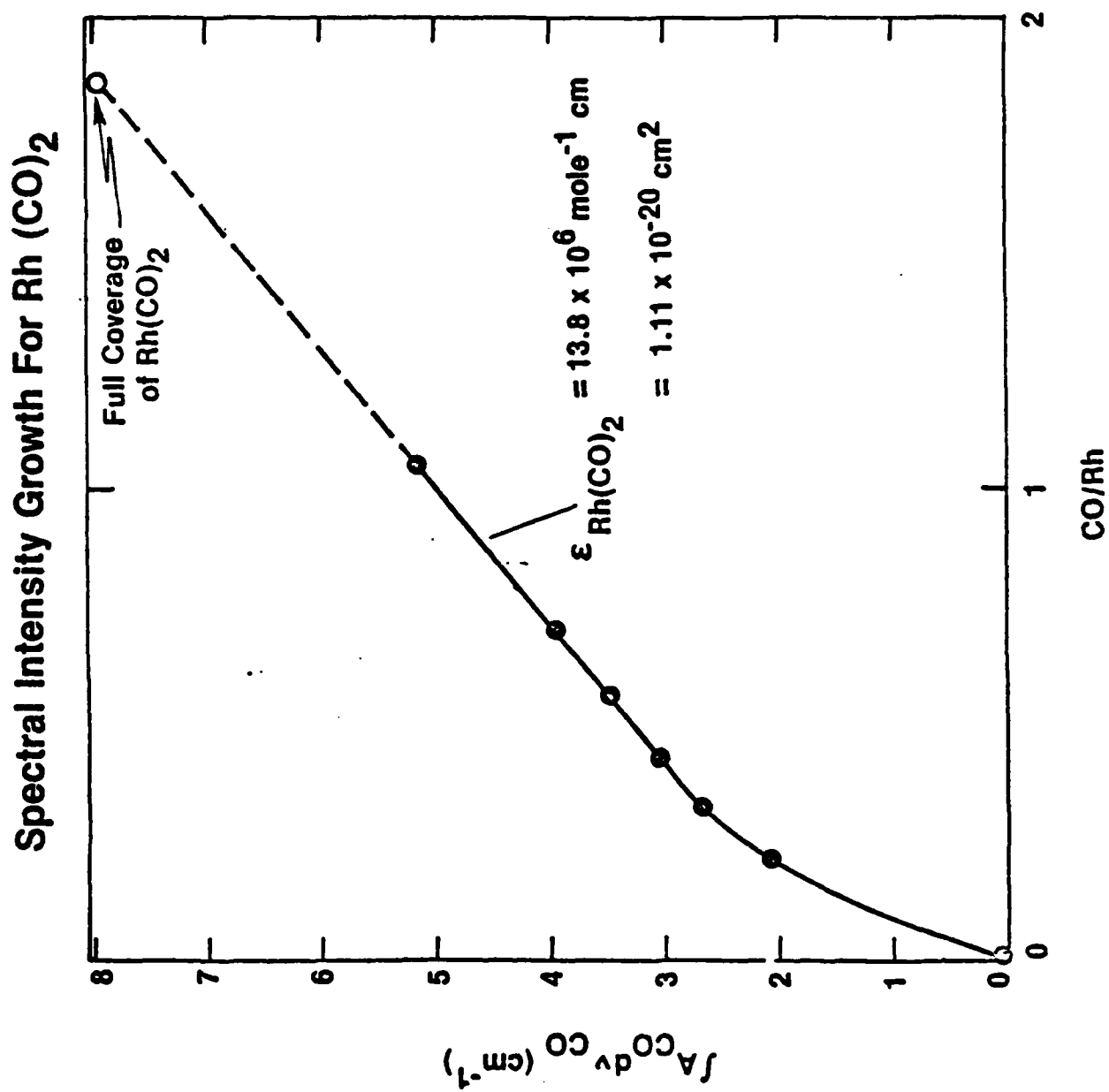Infrared Spectrum of CO Chemisorbed on Rh
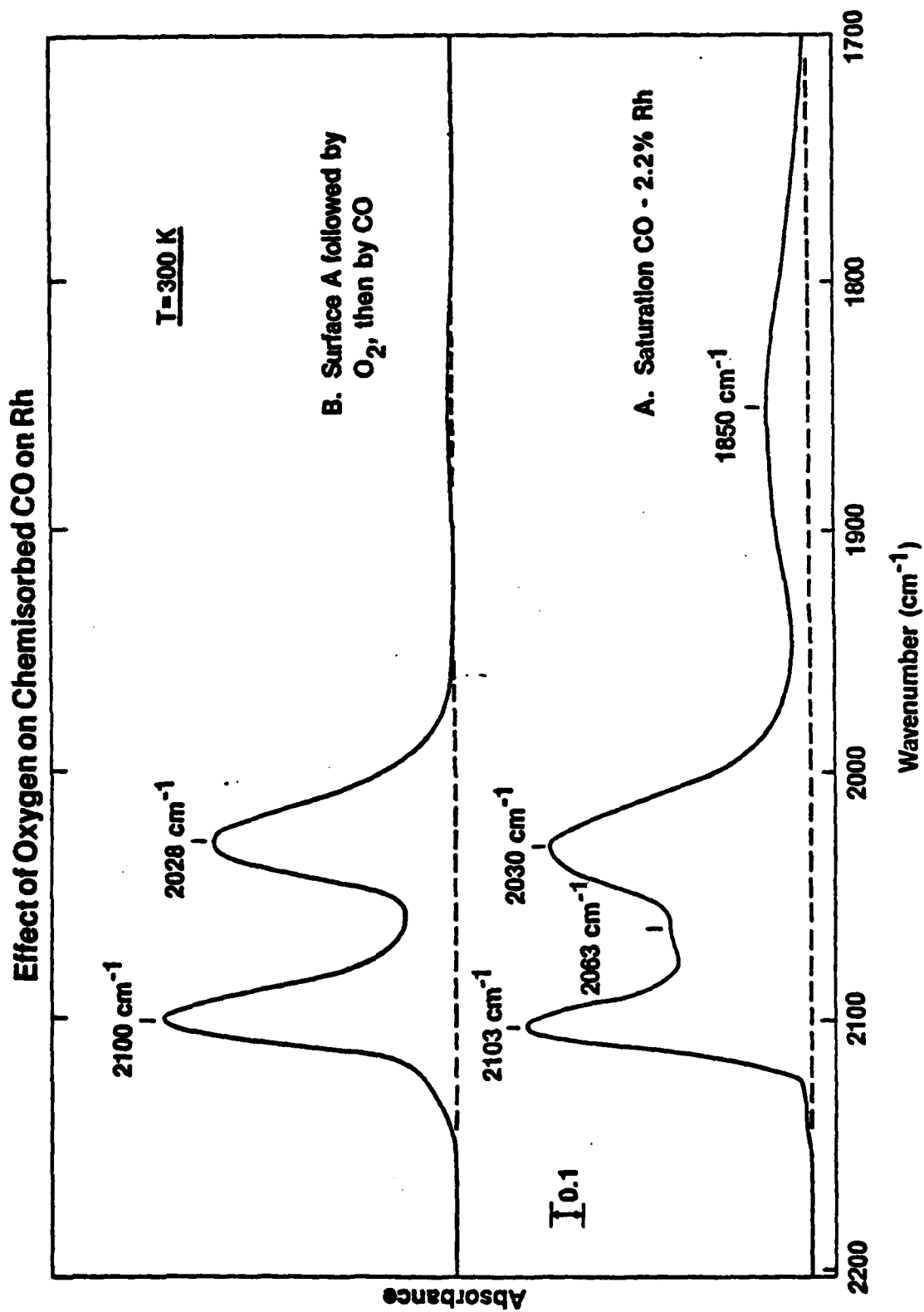
Spectral Intensity Growth For Rh (CO)₂

Full Coverage of Rh(CO)₂

$\varepsilon_{Rh(CO)_2}$ = 13.8 x 10⁶ mole⁻¹ cm

= 1.11 x 10⁻²⁰ cm²

CO/Rh

$\int A_{CO} d\nu_{CO}$ (cm⁻¹)

Figure 2.

Effect of Oxygen on Chemisorbed CO on Rh

T=300 K

B. Surface A followed by O₂, then by CO

2100 cm⁻¹
2028 cm⁻¹

A. Saturation CO - 2.2% Rh

2103 cm⁻¹
2063 cm⁻¹
2030 cm⁻¹
1850 cm⁻¹

0.1

Absorbance

Wavenumber (cm⁻¹)

2200 2100 2000 1900 1800 1700

Figure 3.